Non-equilibrium Thermodynamic Dissolution Theory for Multi-Component Solid/Liquid Surfaces involving Surface Adsorption and Radiolysis Kinetics

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Non-equilibrium Thermodynamic Dissolution Theory for Multi-Component Solid/Liquid Surfaces involving Surface Adsorption and Radiolysis Kinetics

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ABSTRACT: A theoretical expression is developed for the dissolution rate response for multi-component radioactive materials that have surface adsorption kinetics and radiolysis kinetics when wetted by a multi-component aqueous solution. An application for this type of dissolution response is the performance evaluation of multi-component spent nuclear fuels(SNFs) for long term interim storage and for geological disposition. Typically, SNF compositions depend on initial composition, uranium oxide and metal alloys being most common, and on reactor burnup which results in a wide range of fission product and actinide concentrations that decay by alpha, beta, and gamma radiation. These compositional/burnup ranges of SNFs, whether placed in interim storage or emplaced in a geologic repository, will potentially be wetted by multi-component aqueous solutions, and these solutions may be further altered by radiolytic aqueous species due to three radiation fields. The solid states of the SNFs are not thermodynamically stable when wetted and will dissolve, with or without radiolysis. The following development of a dissolution theory is based on a non-equilibrium thermodynamic analysis of energy reactions and energy transport across a solid-liquid phase change discontinuity that propagates at a quasi-steady, dissolution velocity. The integral form of the energy balance equation is used for this spatial surface discontinuity analysis. The integral formulation contains internal energy functionals of classical thermodynamics for both the SNFs' solid state and surface adsorption species, and the adjacent liquid state, which includes radiolytic chemical species. The steady-state concentrations of radiolytic chemical species are expressed by an approximate analysis of the decay radiation transport equation. For purposes of illustration a modified Temkin adsorption isotherm was assumed for the surface adsorption kinetics on an arbitrary, finite area of the solid-liquid dissolution interface. For one of the two models developed, the propagation velocity of the solid-liquid dissolution interface is assumed proportional to configurational entropy discontinuity across the interface. Based on this assumption, the derived functional forms for non-equilibrium rate-thermodynamic force relationships are different from the near-equilibrium, linear rate-thermodynamic force relationships derived from the non-negative entropy dissipation requirement used in the classical approach of Onsager. These analyses of non-equilibrium thermodynamic processes across a propagating discontinuity, along with other idealized dissolution processes that depend on surface adsorption and radiolysis kinetics, provide generic dissolution response functions for empirical and/or regression analysis of data.

Introduction

Most engineering problems involving corrosive dissolution deal with finding a suitable material that has sufficient corrosion resistance when exposed to the expected environmental conditions to met or exceed the design requirements. In most design

situations, the materials' composition is well known, controlled, and stable during service lifetime. The same, or a similar, state of knowledge is often established for the environmental conditions. In a difficult classical design situation, the material selection process may be extended in order to optimize corrosion performance, and the composition of a potential material may be varied in a narrow sense and tests performed over a narrow subset of pre-assigned bounding states of the environmental conditions. The engineering approach is to establish causal relationships for the rate of corrosive dissolution as a function of the variations in the solid material's composition and in the environmental conditions. In idealized and restricted testing cases, and for those situations where an element of good luck plays a deterministic role, causal relationships for dissolution rate data may be relatively simple, and provide support for an intrinsic solid-to-liquid species chemical reaction proposed in a simple stoichiometric relationship. In such cases, this forms and substantiates the basis for a conjectured understanding and mechanistic theory of corrosive dissolution for the given material subjected to the prescribed environmental conditions. However, there are many complex engineering and physically observed corrosive processes for which relationships of dissolution rate data are not simple over a wide subset of multi-variations in the material's composition and the environmental conditions. In these corrosion cases, an applicable generalized understanding and an applicable mechanistic theory are not readily established, nor in most cases possible to establish, using mono-causal concepts and relationships from models and theory of either chemical reaction/transport surface kinetics, or surface adsorption kinetics, or radiolysis kinetics across a surface. In these cases, the reasons for the difficulties in establishing an understanding and a mechanistic theory are usual attributed to a combination, or coupling, of the three classifications of surface kinetics processes. A general analyses for the coupled kinetics of these three surface processes has not been completed. An analysis to couple dissolution and active surface site reactions has been completed[Ref 1], where active sites also addressed precipitation reactions on the surface. The dissolution developments herein will not consider precipitation explicitly, along with its host of kinetics and stoichiometric list of problems. Here, the dissolution developments will extend an initial step to couple the chemical reaction/transport surface kinetics and the surface adsorption kinetics that have been proposed for the dissolution response of uranium dioxide spent nuclear fuels[Ref 2], but some details of that analyses were not fully completed. For processes involving only these two surface kinetics, detailed analyses are being completed elsewhere[Ref 3, 4]. The following section contains a brief theoretical development for dissolution rate response across a multi-component solid/liquid surface that combines interdependent models and theories from all three surface kinetics processes. The theoretical results illustrate multi-causal concepts and relationships from the potential couplings and analytical complexities for dissolution involving the three surface kinetics processes. However, the results also clearly demonstrate why it is that simple stoichiometric relationships are often not experimentally substantiated if the corrosive dissolution processes are coupled to two or three of these surface kinetics processes. Furthermore, if one performs limited tests for dissolution rate data over narrow, mono-variations of prescribed controlled variable conditions for both the material and aqueous compositions, the measured

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mono-subsets of test data may be used to conjecture separate mono-casual relationships in the form of numerical regression models. But the general validity and application of such conjectures, with respect to understanding, mechanism, and uncertainty, should be applied with utmost caution as the mono-casual relationships are not functionally representative of the analytical complexities for dissolution involving multi-surface kinetics processes. Hopefully, the following analyses will attain a level of rigor and clarity to provide both sufficient and necessary reasons to support the statement of caution.

Dissolution Analyses across a Moving Solid/Liquid Interface

Most of the analytical steps in the following are general statements to analyze non-equilibrium thermodynamic dissolution across a generic multi-component solid and liquid interface. However, for purposes of specification of an explicit technical and challenging example in which surface adsorption and radiolysis kinetics are potential influences on the dissolution rate response, the discussion will sometimes be directed to explicit features of uranium spent nuclear fuel contacted by a generic aqueous solution. The objective of the analyses is to obtain function forms for a dissolution rate that are derived from classical thermodynamic, mechanical, and chemical processes across a moving solid/liquid phase change boundary. For the thermodynamics[Ref 5 - 9], the main equation is the quasi-steady rate of energy, work, and heat conservation relationship across the solid-liquid dissolution interface with the solid to liquid energy changes written in terms of the thermodynamic internal energies of the solid and liquid compositions of their initial and subsequent reacted species. For the mechanics[Ref 10 -14], the main equations are the classical mass conservation, kinematics of small deformations, stress equilibrium, electric field-electronic charge, and aqueous radiation-radiolysis species transport equations. For the chemistry[Ref 15 - 20], the main equations are the list of chemical reactions idealized as stoichiometric reactants and products for the surface dissolution species, for the solid site-aqueous species surface adsorption, and for the radiolysis species. In theory, all of these equations are based on well-known concepts and are equal in importance. But in practice, the parametric details of these equations are not known and experimental tests are always required for closure to an application utility. Particularly when the thermodynamic, mechanical, and chemical processes are coupled by spatially inhomogeneous surface reactions and when the number of reactants and products become much over three or four in an environment where temperature and radiation variations are additional boundary conditions.

Since the analyses considers both a solid and adjacent liquid with a moving surface of dissolution between them, explicit definitions for the spatial domains of the solid, the liquid, and the moving dissolution surface are as follows: at time t, the solid body occupies a spatial volume of points x, denoted by $B_S(x, t)$ with its boundary area of spatial points x denoted by $b_S(x, t)$, the adjacent liquid body occupies a spatial volume of points x, denoted by $B_L(x, t)$ with its boundary area of spatial points x denoted by $b_L(x, t)$, and the moving dissolution interface occupies a spatial area of

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points x, denoted by $B_I(x, t)$ with its boundary line of spatial points x denoted by $b_I(x, t)$. For mathematically purposes of writing integral expressions for energy changes, the area set of points $B_I(x, t)$ will be assigned an arbitrarily small, but finite, unit thickness dimensions normal to its centered area surface and treated as if it were a volume set of points between two bounding surface areas in the thickness dimension. Across this thickness dimension, the field functions are assumed continuous; thus, the functions can have different values on the two surfaces of the interface. For example, an electric charge dipole or entropy dipole interface can be analytically represented and would be defined at points {x, t} in $B_I(x, t)$.

Also, in the following dissolution analyses, each set $B_S(x, t)$, $B_L(x, t)$, or $B_I(x, t)$ is assumed materially dense and stochastically continuous, in both the spatial and time domains, with respect to associated, arbitrary subsets {x, t} of finite size contained in their respective interiors as well as up to and on their boundaries. Here, stochastically continuous is a mathematical concept that lets some subsets of the interface area point set $B_I(x, t)$ be represented as probabilistically contiguous to fractional area subsets of both the solid and liquid area boundary sets $b_S(x, t)$ and $b_L(x, t)$ for random sets of time intervals during which a dissolution event occurs. Mechanistically, this provides the mathematical construct for solid species of $B_S(x, t)$ on a subset of $b_S(x, t)$ to dissolve onto an adjacent subset of $b_L(x, t)$ and become liquid species in $B_L(x, t)$, thereby passing through the set $B_I(x, t)$ without a surface adsorption reaction step. These spatial-time subsets of $b_S(x, t)$ and $b_L(x, t)$ are called "direct" solid to liquid dissolution subsets denoted by $b_{SL}(x, t)$. The complement of the "direct" solid to liquid dissolution subsets $b_{SL}(x, t)$ are called "indirect" solid to interface to liquid dissolution spatial-time subsets denoted by $b_{SIL}(x, t)$, and the points {x, t} of $b_{SIL}(x, t)$ identify the subset of stochastic surface areas and time intervals on surface set $B_I(x, t)$ that have adsorption surface reactions. At a random time t, the union, or addition of spatial points in stochastic subsets $b_{SL}(x, t)$ and $b_{SIL}(x, t)$ always equals set $B_I(x, t)$. Furthermore, for observations of dissolution kinetics that leave a smooth(non-pitted) surface at typical macroscopic length and time scales, and which are the assumed conditions for the following analyses of multi-component solids wetted by multi-component liquids, the active solid state lattice sites at which dissolution reactions occur must cyclically cover all points x in set $b_S(x, t)$ during a stochastic time interval determined by the dissolution kinetics. Otherwise, the dissolution reactions would not leave a smooth dissolution surface.

Thermodynamic Energy Equation for a Moving Dissolution Discontinuity

For a moving dissolution surface $B_I(x, t)$, a solid to liquid material phase and compositional discontinuity exists across time varying spatial area subsets, and these

areas must be represented explicitly in coupling the thermodynamics energies of the reacting solid, interface, and liquid species. This coupling is made explicit by using the integral representation for the quasi-steady rate of energy, work, and heat conservation relationship, and mathematically represents the moving dissolution surface as a material discontinuity between point sets $b_S(x, t)$ through stochastic subsets of $B_I(x, t)$ to $b_L(x, t)$. The functional terms for the integral rate of change of energy equation are the thermodynamic internal energy of the solid, per unit mass density, denoted by the functional $E_S(N_S(x, t), M_S(x, t) - M_{So}(x), C_S(x, v_S, t))$; the thermodynamic energy of the liquid denoted by the functional $E_L(N_L(x, t), M_L(x, t), C_L(x, v_L, t))$; thermodynamic energy of the interface denoted by the functional $E_I(N_I(x, t), M_I(x, t), C_I(x, v_I, t))$; the electric field work during charge(current) transport[Ref 12] denoted as the vector inner products $<E_S(x, t), J_S(x, t)>$, $<E_L(x, t), J_L(x, t)>$, and $<E_I(x, t), J_I(x, t)>$; the traction-velocity work rates for the solid, liquid and interface surfaces denoted as vector inner products $<T_S(x, t), v_S(x, t)>$, $<T_L(x, t), v_L(x, t)>$, and $<T_I(x, t), v_I(x, t)>$; and finally the heat flux vectors $h_S(x, t)$, $h_L(x, t)$, and $h_I(x, t)$. The function arguments of the internal energy functionals are the scalar entropy denoted as $N(x, t)$, the small strain tensor denoted as $M(x, t)$, and the concentration(defined as a row matrix) denoted by $C(x, v, t)$ where the vector v is the relative diffusion velocity of a species identified with subscripts for the solid(subscripted S), the liquid(subscripted L), and the interface(subscripted I). The internal energy of the solid is assumed to have a non-zero initial state of strain $M_{So}(x)$ that results from stored mechanical stress-strain work that potentially influences dissolution rates of spent nuclear fuels, particularly for metal alloys that may have fission product and radiation induce damage swelling and/or weld induced stress zones. The energy rate terms that may occur from body forces and body heat generation rates are neglected in this quasi-steady rate analyses, this means that the heat generated by radiation fluxes is explicitly neglected, but is implicitly included in an environmental temperature dependence.

In order to derive explicitly the area influence of the "direct" and "indirect" dissolution surface coupling, the integral form of the energy rate equation is written for arbitrary, but finite subset $B_S(x,t)+b_S(x,t)$ of set $B_S(x,t)+b_S(x,t)$ adjacent to subset $B_I(x,t)+b_I(x,t)$ of set $B_I(x,t)+b_I(x,t)$ adjacent to subset $B_L(x,t)+b_L(x,t)$ of set $B_L(x,t)+b_L(x,t)$. These subsets form a continuous spatial cylinder from the solid through the interface $B_I(x,t)+b_I(x,t)$, which is a volume of small thickness dimension that has one surface adjacent to the solid surface $b_S(x, t)$ and the other surface adjacent to the liquid surface $b_L(x, t)$, and into the liquid subset $B_L(x,t)+b_L(x,t)$. The rate of energy change integrals over volumes and surfaces for each of the three subsets has the form [Ref 2, 5 - 11] :

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$$\int_{B_S} \rho_S \partial_t E_S + <E_S(x, t), \, J_S(x, t) > dB_S + \int_{B_I} \rho_I \partial_t E_I + <E_I(x, t), \, J_I(x, t) > dB_I$$

$$+ \int_{B_L} \rho_S \partial_t E_L + <E_L(x, t), \, J_L(x, t) > dB_L +$$

$$\int_{b_S} \rho_S E_S \, (v_S - V) \cdot n_S + \Delta_{C_s} E_S C_S v_S \cdot n_S - <T_S, \, v_S > - \, h_S \cdot n_S \, db_S +$$

$$\int_{b_I} \rho_I E_I \, (v_I - V) \cdot n_I + \Delta_{C_I} E_I C_I v_I \cdot n_I - <T_I, \, v_I > - \, h_I \cdot n_I \, db_I +$$

$$\int_{b_L} \rho_L E_L \, (v_L - V) \cdot n_L + \Delta_{C_L} E_L \, C_L v_L \cdot n_L - <T_L, \, v_L > - \, h_L \cdot n_L \, db_L = 0 \qquad \text{Eq. 1}$$

This energy equation may be simplified to have only surface integrals for the "direct" and "indirect" dissolution reactions by using a linear functional expansion of the internal energy with respect to its argument functions of entropy **N**, strain **M**, and species composition **C** and by using the divergence theorem. The functional expansion with respect to species composition functions has already been used for the diffusive transport of chemical potential energy through the surfaces of the spatial domains. By using the divergence theorem, the electric field work integrands in the volume integrals can be transformed to the surface integrals provided that: (1). the electric vector **E** can be represented as the spatial gradient of a scalar function $\Phi(x, t)$, thus the vector set $\{E_S, \, E_I, \, E_L \}$ is replaced by $\{\underline{\nabla}\Phi_S, \, \underline{\nabla}\Phi_I, \, \underline{\nabla}\Phi_L \}$, and (2). any transient time rates of change in electric charge density in the volumes are neglected[Ref 12]. These conditions are commonly assumed in electrochemistry[Ref 9]. The work rate and heat flux terms are assumed small, and therefore neglected, for slow rates of dissolution freely exposed to atmospheric pressures. However, a constrained volume dissolution reaction may create significant pressures in the liquid and solid because of the potential density decrease across the dissolution discontinuity. From this discussion, the energy rate equation on stochastic surface subsets $b_{SL}(x, t)$ and $b_{SIL}(x, t)$ across the material phase discontinuity moving at an averaged velocity **V** is reduced to:

$$\int_{b_{SL}} \rho_S [\Delta_{N_S} E_S \, N_S + \Delta_{M_S} E_S \, (M_S - M_{So}) + \Delta_{C_s} E_S C_S](v_S - V) \cdot n_S$$

$$+ \rho_L [\Delta_{N_L} E_L \, N_L + \Delta_{M_L} E_L \, M_L + \Delta_{C_L} E_L C_L \,](v_L - V) \cdot n_L$$

$$+ \rho_S \, \Delta_{C_s} E_S C_S v_S \cdot n_S + \rho_L \, \Delta_{C_L} E_L C_L v_L \cdot n_L + J \cdot (\Phi_S n_S + \Phi_L n_L) db_{SL} +$$

$$\int_{b_{SIL}} \rho_S[\Delta_{N_S} E_S \, N_S + \Delta_{M_S} E_S \, (M_S - M_{So}) + \Delta_{c_S} E_S C_S](v_S - V) \cdot n_S$$

$$+ \; \rho_S \, \Delta_{c_S} E_S C_S v_S \cdot n_S + \rho_I \, \Delta_{C_I} E_I C_I v_I \cdot n_{IS} + J \cdot (\Phi_S n_S + \Phi_{IS} n_{IS})$$

$$+ \; \rho_I [\Delta_{N_I} E_I \, N_I + \Delta_{M_I} E_I \, M_I + \Delta_{C_I} E_I C_I](v_I - V) \cdot n_{IS}$$

$$+ \; \rho_I [\Delta_{N_I} E_I \, N_I + \Delta_{M_I} E_I \, M_I + \Delta_{C_I} E_I C_I](v_I - V) \cdot n_{IL}$$

$$+ \; \rho_I \, \Delta_{C_I} E_I C_I v_I \cdot n_{IL} + \rho_L \, \Delta_{C_L} E_L C_L v_L \cdot n_L + J \cdot (\Phi_{IL} n_{IL} + \Phi_L n_L)$$

$$+ \; \rho_L[\Delta_{N_L} E_L \, N_L + \Delta_{M_L} E_L \, M_L + \Delta_{C_L} E_L C_L](v_L - V) \cdot n_L \; db_{SIL} = 0 \quad \text{Eq. 2}$$

The first integral of Eq. 2 is descriptive of the internal energy change as the solid species at an entropy state of N_S, at a strain state of $(M_S - M_{So})$, and at a chemical potential energy state of $\Delta_{c_S} E_S$, dissolve "direct form solid to liquid" at a mass flux rate of $\rho_S(v_S - V) \cdot n_S$ at points on the moving dissolution boundary $b_{SL}(x, t)$ and become aqueous species at an entropy state of N_L, at a strain state of M_L, and at a chemical potential energy state of $\Delta_{c_L} E_L$ at a mass flux rate of $\rho_L(v_L - V) \cdot n_L$, plus the energy rate from diffusive transported solid and aqueous species and the energy from the charge transport(current J) across the charge layers at the surfaces of the solid and the adjacent liquid. Certainly, the mass flux at the solid surface must equal the mass flux at the adjacent liquid surface, and neglecting the diffusive mass fluxes this implies that $\rho_S(v_S - V) \cdot n_S$ equals $\rho_L(v_L - V) \cdot n_L$, where the unit normal vector n_S of the solid is directed outward from the solid toward the liquid and the unit normal vector n_L of the solid is in the opposite direction to the n_S unit normal vector of the solid. As the solid dissolves, it will be assumed that the solid particle velocity v_S is zero, thus the dissolution mass rate is $-(\rho_S V \cdot n_S)$, which is a positive value as the dissolution velocity vector is pointed into the solid. If the solid and liquid density were the same, then the liquid particle velocity would be zero. This is not typically the case so the liquid velocity v_L is not zero in most cases. However, it may be evaluated for the case of v_S equal to zero by equating the solid and liquid mass fluxes and using $n_S = - n_L$ as follows, and the result will be used later to simplify an equation for theoretical function models of dissolution.

$$\rho_L(v_L - V) \cdot n_L = \rho_S(v_S - V) \cdot n_S = -\rho_S \, V \cdot n_S = \rho_S \, V \cdot n_L \qquad \text{Eq. 3a}$$

$$v_L \cdot n_L = -V \cdot n_S - \rho_S \, V \cdot n_S / \rho_L \qquad \text{Eq. 3b}$$

Chemical Potential Energy and Effective Stoichiometric Coefficients

The chemical potential terms of the solid species in the first integral of Eq. 2 are for each of the chemical components in the solid, which for a spent fuel would number in the hundreds when the fission products and actinides are considered. However, the experimental or first principles' task of isolating and assigning a dissolution response to particular, or even a subset of these SNF chemical components is not presently possible. But using existing classical thermodynamic forms of the chemical potential function, it is in theory correct to assign the aggregate variable of spent fuel burnup as a casual metric to explain some observations in the variations of dissolution test data with corresponding variation in test samples of different SF burn-up. To derive the dependence of SF burn-up as an aggregate variable, start with the chemical potential for small atomic concentrations in a solid state lattice, which is typically given as[Ref 5-9]

$$\Delta_{C_S} E_S = \mu_s = \mu_{so} + kT\ln[C_S] \qquad\qquad \text{Eq. 4}$$

where μ_{so} is the standard state value of chemical potential at a normalized standard state concentration value of $[C_S]$ normalized to one and "k" is Boltzmann's constant. The in-reactor fission products concentrations, and most all actinide concentrations, increase at a linear proportionality with the unit measure of SF burn-up for a given neutron energy spectrum in a reactor. Thus, letting the variable **Bu** denote a measure of fissions per cc of fuel burn-up and the parameter K_S denote the proportionality constant for a given solid state fission product or actinide species S, the SF solid state concentration for species S is given by

$$[C_S] = K_S\, \textbf{Bu} \qquad\qquad \text{Eq. 5}$$

The expression in Eq. 2 for the chemical potential energy of the solid state is given by $\Delta_{C_S} E_S C_S$, where the value of C_S is the amount(atoms or moles) of species S that is reacted per unit of solid mass flux $\rho_S(v_S - V)\bullet n_S$. If the variable C_S is normalized by the moles or atoms(per unit mass) of the SF matrix material C_{SF} that is reacting, then C_S/C_{SF} defines a set of effective stoichiometric coefficients c_S for the species S in the solid state. Then the chemical potential energy for the solid state fission products and actinide species in Eq. 2, combined with Eq. 4 and Eq. 5, can be written as(note that the term $\Delta_{C_S} E_S C_S$ denotes a summation of the product of the chemical potential for each species S and an amount C_S of that species over all solid state species):

$$\Delta_{C_S} E_S C_S = \mu_s C_S = (\mu_{so} + kT\ln[C_S])\, C_S = ((\mu_{so} + kT\ln[C_S])\, c_S)\, C_{SF}$$

$$= ((\mu_{so} + kT\ln[K_S\, \textbf{Bu}])\, c_S)\, C_{SF} = (\mu_{so}\, c_S + kT\ln[K_S\, \textbf{Bu}]^{c_S})C_{SF}$$

$$= (\mu_{so}c_S + kTln[K_S]^{C_S} + kTln[\mathbf{Bu}]^{C_S}) \, \mathbf{C}_{SF}$$

$$= (\mu_{so}c_S + kTln[K_S]^{C_S} + \{c_S\}kTln[\mathbf{Bu}]) \, \mathbf{C}_{SF} \qquad \text{Eq. 6}$$

where the algebraic rules for logarithmic functions were used to show the coupled chemical potential energy of all solid state burn-up induced species is linear in ln(**Bu**), as the coefficient $\{c_S\}$ of kTln(**Bu**) is just the sum over the set of effective stoichiometric coefficients c_S for the direct dissolution reaction of a unit amount $\mathbf{C}_{SF}$ of SF. The same type of analysis can be performed for the reacted product species of the spent fuel in the aqueous solution. However, the aqueous solution will not only contain the SF solid to liquid ionic species denoted by $\mathbf{C}_{SL}$, but in addition the liquid also has the initial state of aqueous species denoted by $\mathbf{C}_A$, and the aqueous radiolysis species denoted by $\mathbf{C}_R$. Thus, spent fuel to liquid reaction products from reactions with the SF solid and the initial state of aqueous species will create new solid-aqueous species $\mathbf{C}_{SA}$. And spent fuel to liquid reaction products from reactions with the SF solid and the aqueous radiolysis species will create solid-aqueous radiolysis species $\mathbf{C}_{SR}$. Thus, the liquid state composition matrix $\mathbf{C}_L$ has subsets of species $\mathbf{C}_A$, $\mathbf{C}_R$, $\mathbf{C}_{SL}$, $\mathbf{C}_{SA}$, and $\mathbf{C}_{SR}$. For only the reacted SF ionic species subset $\mathbf{C}_{SL}$ in the aqueous solution, a liquid induced burn-up dependence on fission product and actinide species can be derived analogously to Eq. 6, and is given by:

$$\Delta_{c_{SL}}E_L\mathbf{C}_{SL} = \mu_{SL}\mathbf{C}_{SL} = (\mu_{SLo}c_{SL} + kTln[K_{SL}]^{C_{SL}} + \{c_{SL}\}kTln[\mathbf{Bu}])\mathbf{C}_{SF} \quad \text{Eq.7}$$

where changes in the aqueous reacted product species identities(for example lattice atoms to ions), solid concentrations ($K_S\mathbf{Bu}$) to liquid concentrations ($K_{SL}\mathbf{Bu}$), and their associated aqueous chemical potentials will occur. Hence, the subscripts of Eq. 7 are changed to reflect this over the subset of aqueous effective stoichiometric coefficients c_{SL} and on their associated aqueous chemical potentials, but the coupled chemical potential energy of all solid state burn-up induced species dissolved as ions into the liquid remains linear in ln(**Bu**) for only the direct ionic dissolution reaction of a unit amount $\mathbf{C}_{SF}$ of SF. However, by controlling the relative aqueous concentrations of these reacted product species during dissolution testing by variations in the set K_{SL}, one can isolate and assign a potential SF species effect to a solid state dissolution response or an aqueous dissolution response. This assumes that any surface adsorption and radiolysis kinetics effects can be isolated by testing and are shown to be negligible in comparison. As will be discussed in the following, the latter two effects are not readily isolated.

A simplified surface adsorption that is coupled to the dissolution energy rate can be completed from a reduced form of Eq. 2. For this reduced form of Eq. 2,

it will be assumed that the diffusive transport is not a limiting process, this is a good assumption for flow-through dissolution tests, so the terms with diffusion velocity v are eliminated from Eq. 2. In addition, it will be assumed that the electro-chemical energy contribution can be neglected, so the terms with charge transport J are eliminated from Eq. 2. This assumption need not be made, but it greatly shortens the analysis. Finally, the above discussions and Eqs. 3 through 7 are used to re-arrange and write Eq. 2 more compactly as:

$$\int_{b_{SL}} \{ [\Delta_{N_L} E_L N_L + \Delta_{M_L} E_L M_L + \mu_L C_L]$$

$$- [\Delta_{N_S} E_S N_S + \Delta_{M_S} E_S (M_S - M_{So}) + \mu_S c_S C_{SF}] \} (\rho_S V) \cdot n_L \, db_{SL} +$$

$$\int_{b_{SIL}} \{ [\Delta_{N_S} E_S N_S + \Delta_{M_S} E_S (M_S - M_{So}) + \mu_S c_S C_{SF}] \} (- \rho_S V) \cdot n_L$$

$$+ [\Delta_{N_L} E_L N_L + \Delta_{M_L} E_L M_L + \mu_L C_L] (\rho_S V) \cdot n_L$$

$$+ \rho_I [\Delta_{N_I} E_I N_I + \Delta_{M_I} E_I M_I + \Delta_{C_I} E_I C_I](v_I - V) \cdot n_{IS}$$

$$+ \rho_I [\Delta_{N_I} E_I N_I + \Delta_{M_I} E_I M_I + \Delta_{C_I} E_I C_I](v_I - V) \cdot n_{IL} \, db_{SIL} = 0 \quad \text{Eq. 8}$$

The simplification of Eq. 2 to Eq. 8 still leaves terms that can be reasonable be neglected and others, such as the two interface terms, mass flux and chemical potential energy, and the aqueous radiolysis chemical potential energy terms $\mu_R C_R$, that will require additional analyses. For example, the strain energy densities for the liquid and the interface surface can be assumed negligible at low pressures. Also, any change in the solid strain M_S from the initial strain value of M_{So}(as the solid particle velocity was assumed to be zero at the dissolution front) will be neglected, but the initial strain energy density of the solid will be retained. For the mass flux term, consider first that the two interface terms for surface adsorption processes have unit normal vectors, n_{IS} pointed toward the solid, and n_{IL} pointed toward the liquid; the vector n_{IS} is equal to n_L and the n_{IL} is equal to minus n_L. Secondly, the mass flux across both surfaces of the interface is equal to solid dissolution mass flux. Furthermore, the thickness of this idealized interface has been assumed constant, thus, the normal particle velocity of the interface must be zero. The interface is attached to and moves with the dissolution front at velocity V. Based on this, the mass density of the idealized interface must equal that of the solid. Then, a single mass flux multiplier, $\rho_S V \cdot n_L$, determined in Eq. (3a) can be used for all terms in both integrands of Eq. 8. This leaves the entropy energy and the chemical potential energy terms of the interface to simplify. The entropy energy terms across the adsorption interface are simplified in the context of the

previous assumption that assumed dipole-like field functions in the thickness direction of the interface. Hence, the interface entropy function may have different values on the two idealized surfaces of the interface. This dipole-like interface entropy function means that discontinuities across the surface of the solid and interface and across the surface of the interface and liquid can be functionally represented. Thus, "thermodynamically reversible" and "irreversible" adsorption processes can be represented. For these adsorption processes, imagine one was on the mid-surface of the interface and looked in the direction of the solid, which is the positive direction of unit vector n_L, stochastic fields of entropy and chemical potential functions associated with the solid surface and those of interface would be seen. The stochastic fields of entropy and chemical potential functions of the interface are the existing n_{IS} coefficient terms in the interface integrand. Similarly, if one were looking in the direction of the liquid, which is also the negative direction of unit vector n_L, stochastic fields of entropy and chemical potential functions associated the liquid surface and those of interface would be seen. The stochastic fields of entropy and chemical potential functions of the interface are the existing n_{IL} coefficient terms in the interface integrand. Thus, the interface has a set of entropy and chemical potential energies $\Delta_{N_I} E_I \, N_I + \Delta_{C_I} E_I C_I$ on the solid side which will be denoted as positive $(\Delta_{N_{IS}} E_{IS} \, N_{IS} + \Delta_{C_{IS}} E_{IS} C_{IS})n_L$. Similarly, the interface also has a set of entropy and chemical potentials energies on the liquid side which will be denoted as negative $(\Delta_{N_{IL}} E_{IL} \, N_{IL} + \Delta_{C_{IL}} E_{IL} C_{IL})n_L$. The positive and negative values for these energies are assigned because a common unit normal vector n_L is used as a directional attribute to consistently represent contributions to the values of the integrals from function discontinuities across moving surfaces. The physical concept is that a propagating chemical reaction front, i.e., the dissolution phase change process, has a chemical potential energy change; this chemical energy is transformed into an entropy energy change so that the net energy change is zero. Hence, energy is conserved by transformations of admissible subsets of energy as required by the first law of thermodynamics.

From this discussion, Eq. 8 can be further simplified and re-written as an entropy energy production integration equal to integrals for strain energy and chemical potential energy change as the dissolution front propagates at velocity **V** as follows:

$$\int_{b_{SL}} \{[\Delta_{N_L} E_L N_L - \Delta_{N_S} E_S N_S] \, (\rho_S \, V) \cdot n_L\} \, db_{SL} \quad +$$

$$\int_{b_{SIL}} \{[\Delta_{N_L} E_L N_L - \Delta_{N_{IL}} E_{IL} N_{IL} + \Delta_{N_{IS}} E_{IS} N_{IS} - \Delta_{N_S} E_S N_S](\rho_S V) \cdot n_L\} \, db_{SIL} \quad =$$

$$- \int_{b_{SL}} \{[\mu_L C_L - \Delta_{M_S} E_S(- M_{So}) - \mu_S c_S C_{SF}](\rho_S V) \cdot n_L\} \, db_{SL}$$

$$- \int_{b_{SIL}} \{ [\mu_L C_L - \Delta_{C_{IL}} E_{IL} C_{IL}$$

$$+ \Delta_{C_{IS}} E_{IS} C_{IS} - \Delta_{M_S} E_S(- M_{So}) - \mu_S c_S C_{SF}](\rho_S V) \cdot n_L\} \, db_{SIL} \qquad \text{Eq. 9}$$

The above Eq. 9 shows clearly that the entropy energy rate is equal to minus the chemical energy and strain energy rates as the dissolution reaction front propagates. Since a chemical reaction only continues to occur for a decrease in the thermodynamic energy from the initial state(the solid state reactants) to the final state(the solid direct and indirect dissolution paths to aqueous species products), the minus sign means that the right-side is positive for solid dissolution, since $(\rho_S V) \cdot n_L$ is then positive. For a non-equilibrium Onsager model, the positive-definite entropy production rate requirement expressed in terms of the function N and $(\rho_S V) \cdot n_L$ would be used to conjecture a near thermodynamic equilibrium dissolution model. As an example of an Onsager model, an initial conjecture might be that the averaged dissolution rate, $(\rho_S V_{AVE}) \cdot n_L$, is equal to a linear coefficient matrix (or a linear functional) multiplied by the chemical energy and strain energy terms in the square brackets on the right hand-side of Eq. 9. This type of linear model approaches zero dissolution rates as the thermodynamic driving force, which in this case would be the chemical energy of the reaction step, approaches zero. Another possibility is to assume a non-equilibrium model such that the dissolution process is far from thermodynamic equilibrium, and that it does not attain equilibrium until the reactants are consumed. Such a model was assumed for SF uranium oxide dissolution[Ref 2], and was based on the conjecture that the thermodynamic driving force was the configuration entropy, rather than the chemical energy. Both types of models would require experiments to establish the coefficient matrices, and a subset of effective stoichiometric coefficients for the reaction steps. This experimental requirement is true for most all non-equilibrium models that use classical thermodynamic methodologies. Before any further discussion of these types of non-equilibrium models, Eq. 9 must be written such that the full set of effective stoichiometric coefficients for the reaction steps are defined and explicitly identified as per unit mass of the soild.

Previously, sets of effective stoichiometric coefficients, c_S, were defined for the solid species, and solid to liquid ionic species products, c_{SL}, in Eqs. 6 and 7. A full aqueous set of effective stoichiometric coefficients, c_L, would also includes coefficient sets of initial aqueous species and its reacted solid products, and coefficient sets of aqueous radiolysis species and its reacted solid products. The explicit development of set c_L to include these other reactions will use a similar conceptual approach to that used for the solid to aqueous ionic species

and will be such that the units are sets of effective stoichiometric coefficients per unit amount C_{SF} of spent fuel. In order to define a set of effective stoichiometric coefficients for solid species and initial aqueous liquid state reactions, c_{SA}, consider the chemical potential energy change ΔE for an arbitrary solid species(of amount $C_S = c_S C_{SF}$) and an arbitrary initial aqueous liquid state species C_A reaction from which aqueous product concentrations, C_{SA}, are formed. This energy is expressed as:

$$\Delta E(C_S + C_A \Leftrightarrow C_{SA}) = \Delta_{C_{SA}} E_L C_{SA} - (\Delta_{C_S} E_S C_S + \Delta_{C_A} E_L C_A)$$

$$= (\Delta_{C_{SA}} E_L c_{SA} - (\Delta_{C_S} E_S c_S + \Delta_{C_A} E_L c_A)) C_{SF} \qquad \text{Eq. 10}$$

which is the energy change for a stoichiometric reaction of $c_S C_{SF}$ atoms or moles per unit spent fuel mass of a solid species "S" with an initial aqueous liquid species "A" (of amount $C_A = c_A C_{SF}$) and forms an aqueous reaction product species "SA"(of amount $C_{SA} = c_{SA} C_{SF}$). Thus, the set of effective stoichiometric coefficients $\{c_S, c_A, c_{SA}\}$ are normalized per unit amount C_{SF} of spent fuel. A similar energy equation can be written for an arbitrary solid species C_S and an arbitrary aqueous radiolysis species C_R reaction to form aqueous radiolysis species reaction products C_{SR}, namely;

$$\Delta E(C_S + C_R \Leftrightarrow C_{SR}) = \Delta_{C_{SR}} E_L C_{SR} - (\Delta_{C_S} E_S C_S + \Delta_{C_R} E_L C_R)$$

$$= (\Delta_{C_{SR}} E_L c_{SR} - (\Delta_{C_S} E_S c_S + \Delta_{C_R} E_L c_R)) C_{SF} \qquad \text{Eq. 11}$$

which defines a set of effective stoichiometric coefficients $\{c_S, c_R, c_{SR}\}$ that are normalized per unit amount C_{SF} of spent fuel. The remaining reactions to describe and to normalize are the surface adsorption reactions on the solid side of the interface and on the liquid side of the interface that are expressed in Eq. 9 by the interface chemical potential energies, $\Delta_{C_{IS}} E_{IS} C_{IS}$ and $\Delta_{C_{IL}} E_{IL} C_{IL}$. For a conceptual solid-interface model for solid-interface species C_{IS}, consider an arbitrary solid species C_S that has a surface reaction with any existing, or combination of the aqueous species C_L in subset $\{C_A, C_R, C_{SL}, C_{SA}, C_{SR}\}$ to form an interface species C_{IS}. The chemical energy of this generic reaction can be expressed and normalized similarly to that of Eq. 10, which is:

$$\Delta E(C_S + C_A + C_R + C_{SL} + C_{SA} + C_{SR} \Leftrightarrow C_{IS}) = \Delta_{C_{IS}} E_{IS} C_{IS} - (\Delta_{C_S} E_S C_S$$

$$+ \Delta_{C_A} E_L C_A + \Delta_{C_R} E_L C_R + \Delta_{C_{SL}} E_L C_{SL} + \Delta_{C_{SA}} E_L C_{SA} + \Delta_{C_{SR}} E_L C_{SR})$$

$$= (\Delta_{C_{IS}} E_{IS} c_{IS} - (\Delta_{C_S} E_S c_S + \Delta_{C_A} E_L c_A + \Delta_{C_R} E_L c_R + \Delta_{C_{SL}} E_L c_{SL} +$$

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$$\Delta_{C_{SA}}E_L c_{SA} + \Delta_{C_{SR}}E_L c_{SR}))C_{SF} \qquad \text{Eq. 12}$$

Eq. 12 defines the set of effective stoichiometric coefficients $\{c_S$, c_A , c_R , c_{SL} , c_{SA} , c_{SR}, $c_{IS}\}$ for the solid-interface product species C_{IS}. These coefficients are normalized per unit amount C_{SF} of spent fuel because the primary reactant is a solid species C_S. An energy equation similar to Eq. 12 can be written for the liquid-interface product species C_{IL} to define its associated coefficients. These reactions are between the solid-interface species C_{IS} and any existing, or combination of the aqueous species C_L in subset $\{C_A$, C_R , C_{SL} , C_{SA} , $C_{SR}\}$, thus, the chemical energy expression is:

$$\Delta E(C_{SI} + C_A + C_R + C_{SL} + C_{SA} + C_{SR} \Leftrightarrow C_{IL}) = \Delta_{C_{IL}}E_{IL}C_{IL} - (\Delta_{C_{IS}}E_{IS}C_{IS}$$

$$+ \Delta_{C_A}E_L C_A + \Delta_{C_R}E_L C_R + \Delta_{C_{SL}}E_L C_{SL} + \Delta_{C_{SA}}E_L C_{SA} + \Delta_{C_{SR}}E_L C_{SR})$$

$$= (\Delta_{C_{IL}}E_{IL}c_{IL} - (\Delta_{C_{IS}}E_{IS}c_{IS} + \Delta_{C_A}E_L c_A + \Delta_{C_R}E_L c_R + \Delta_{C_{SL}}E_L c_{SL} +$$

$$\Delta_{C_{SA}}E_L c_{SA} + \Delta_{C_{SR}}E_L c_{SR}))C_{SF} \qquad \text{Eq. 13}$$

Eq. 13 defines the set of effective stoichiometric coefficients $\{c_{IS}$, c_A , c_R , c_{SL} , c_{SA} , c_{SR}, $c_{IL}\}$ for the solid-interface product species C_{IS}. These coefficients are normalized per unit amount C_{SF} of spent fuel because the primary reactant is a member of the solid-interface species C_{IS}. And the solid-interface species C_{IS} were shown with Eq. 12 to be related to the solid species C_S, therefore, the set of effective stoichiometric coefficients $\{c_{IS}$, c_A , c_R , c_{SL} , c_{SA} , c_{SR}, $c_{IL}\}$ are also normalized per unit amount C_{SF} of spent fuel.

Surface Adsorption Kinetics and a Generalized Temkin Isotherm

This completes the definitions and developments for the full set of effective stoichiometric coefficients for all the reaction steps that will be considered, in a theoretical sense, as contributions to the entropy energy and the chemical energy across a moving dissolution front of Eq. 9. In a practical sense, and fortunately for most engineering applications, the number of significant corrosive dissolution reactions are usually related to only a few additive element components in the solid and a few component species of the liquid environment. This leads to the value of a formally derived and intrinsically consistent theoretical model, which in some cases will have a dependence on temperature and radiolysis. With such a model, a reasonable and efficient experimental approach can be planned and performed for sufficient data to establish empirical values for only a subset of the significant parameters. For example, a plan of tests designed to evaluate only a subset of the full set of effective stoichiometric coefficients to isolate the influence of a few components in the solid and/or liquid, and environmental temperature and radiolysis effects.

To derive such a model from Eq. 9, the above definitions of effective stoichiometric coefficients for all the reaction steps must be used in order to show and thereby clarify the normalized energy change per unit of spent fuel. Also, the definition of thermodynamic temperature, which is the variation of the internal energy functional with respect to the entropy function, $T = \Delta_{N_L} E_L$, will be used to reduce the entropy energy terms for all energy functionals of the solid, the interface, and the liquid. Here, it has been assumed that the dissolution front is moving quasi-steady, so that a uniform temperature across the dissolution front, solid to interface to liquid, is a reasonable approximation. Finally, the positive definite strain energy density term $\Delta_{M_S} E_S(- \mathbf{M}_{So})$ per unit mass of the solid will be replaced with the shorten notation of $\Delta E_S(\mathbf{M}_{So})\mathbf{C}_{SF}$, which normalizes the strain energy density per unit atom or mole of the solid, the notation, μ_{IS} and μ_{IL}, will replace the chemical potentials, $\Delta_{c_{IS}} E_{IS} \mathbf{C}_{IS}$ and $\Delta_{c_{IL}} E_{IL} \mathbf{C}_{IL}$, the notation μ_{LA}, μ_{LR}, μ_{LSL}, μ_{LSA}, and μ_{LSR}, will be used to replace the liquid's chemical potentials of the separate species subsets as written in Eqs. 12 and 13 (which is equivalent to the notation $\mu_L \mathbf{C}_L$ used previously in Eq. 9). With the discussed substitutions and notational changes for chemical potentials, Eq. 9 can be re-written as:

$$\int_{b_{SL}} \{ T\,[\mathbf{N}_L - \mathbf{N}_S]\,(\rho_S\mathbf{V})\bullet\mathbf{n}_L \}\,db_{SL} \;+$$

$$\int_{b_{SIL}} \{ T\,[\mathbf{N}_L - \mathbf{N}_{IL} + \mathbf{N}_{IS} - \mathbf{N}_S](\rho_S\mathbf{V})\bullet\mathbf{n}_L \}\,db_{SIL} \;=$$

$$-\int_{b_{SL}} \{[\mu_{LA}c_A + \mu_{LR}c_R + \mu_{LSL}c_{SL} + \mu_{LSA}c_{SA} + \mu_{LSR}c_{SR} - \Delta E_S(\mathbf{M}_{So})$$

$$-\;\mu_S c_S]\, \mathbf{C}_{SF}(\rho_S\mathbf{V})\bullet\mathbf{n}_L\,db_{SL}$$

$$-\int_{b_{SIL}} \{\, [\mu_{LA}c_A + \mu_{LR}c_R + \mu_{LSL}c_{SL} + \mu_{LSA}c_{SA} + \mu_{LSR}c_{SR} - \mu_{IL}c_{IL}$$

$$+\;\mu_{IS}c_{IS} - \Delta E_S(\mathbf{M}_{So}) - \mu_S c_S\,]\, \mathbf{C}_{SF}(\rho_S\mathbf{V})\bullet\mathbf{n}_L\}\,db_{SIL} \qquad \text{Eq. 14}$$

The function form of Eq. 14 has two pairs of surface integrals, one pair over surface b_{SL} for "direct" dissolution processes and the other over surface b_{SIL} for "indirect" dissolution processes. At a practical and applications' level, an averaged velocity $(V_{AVE})\bullet n_L$ or averaged mass flux $(\rho_S V_{AVE})\bullet n_L$ measure of corrosive dissolution is a minimal requirement to deduce from Eq. 14. Any additional detailed understanding are requirements to address issues in understanding, rigor, clarity, and certainty. In view of the latter, note that each

integral has different functions forms for integrands, however, in the derivations leading to Eq. 14, the dissolution front and its propagation velocity $\mathbf{V} \bullet \mathbf{n}_L$ were assumed spatially continuous at a typical observable length scale(no pitting assumption). This continuity is not, however, true at micro-scales of length and time since $\mathbf{V} \bullet \mathbf{n}_L$ is potentially very different at point x in subset b_{SL} relative to a neighborhood point in subset b_{SIL}. Thus, the point dependent velocity $\mathbf{V} \bullet \mathbf{n}_L$ can not be factored outside of the integrals. In fact, to perform the integrations, the stochastic dependence of a surface point x belonging to surface solid subset b_{SL} or surface interface subset b_{SIL} at a particular time or even during a prescribed time interval is necessary[Ref 4, 21]. This is the fundamental statistical nature of surface adsorption kinetics[Ref 1, 17-18], and the integration to couple adsorption and dissolution kinetics is stochastic in that the probability of a point (x,t) belonging to subset b_{SL} or subset b_{SIL} is an intrinsic functional dependence of the integration over the dissolution surface set b_I, which is equal to subset b_{SL} plus subset b_{SIL}. The detailed mathematical and mechanistic problems can be resolved by assuming that the stochastic processes of placing a point (x,t) in subset b_{SL} or subset b_{SIL} at some time t are *asymptotically stationary* with respect to time intervals on arbitrary observable time scales[Ref 4, 21]. This assumption is essential to the use of classical adsorption isotherms, such as a Langmuir, a Freundlich, or a Temkin isotherm, and to assign the probable proportionality of surface point subsets to the "direct and indirect" dissolution pathways. As a example, the Temkin isotherm[Ref 18] will be used to illustrate the coupling adsorption and dissolution kinetics in Eq.14. The Temkin isotherm is considered a reasonable approximation to assign indexes θ_{SIL} of probable proportional surface coverage on set b_I by adsorption in the mid-range, i.e., away from end points of near zero coverage, $\theta_{SIL} \sim 0$, and near full coverage, $\theta_{SIL} \sim 1$. The equation form of a Temkin isotherm is species concentration dependent, and for a single aqueous species [C] and a given surface composition, has an analogous form[Ref 18] to that of the chemical potential functions in Eq. 4, namely:

$$\theta_{SIL} = p_{SIL0} + p_{SIL}kTln[C] \qquad \text{Eq. 15}$$

where values for the interface parameters p_{SIL0} and p_{SIL} are usually estimated from test data for a prescribed surface and a range of solution concentrations. For this analysis of multi-component solid and liquid concentrations, $\mathbf{C_S}$ and $\mathbf{C_L}$, it is assumed that a general, linearly additive(superposition) form of Eq. 15 will adequately approximate a multi-component Temkin adsorption isotherm. This generalized form, with parameter subsets $\{p_{SI0}, p_{SI}, p_{IL0}, p_{IL}\}$, is expressed by:

$$\theta_{SIL} ([\mathbf{C_S}], [\mathbf{C_L}]) = p_{SI0} + p_{SI}kTln[\mathbf{C_S}] + p_{IL0} + p_{IL}kTln[\mathbf{C_L}] \qquad \text{Eq. 16}$$

Using Eq. 16, the surface subset b_{SL} and subset b_{SIL} of the dissolution interface set b_I will be deterministically proportioned as:

$$b_{SL} = (1 - \theta_{SIL}) \, b_I \quad \text{and} \quad b_{SIL} = \theta_{SIL} \, b_I \qquad \text{Eq. 17}$$

Furthermore, this implies that the arbitrary surface subset b_{SL} and subset b_{SIL} of the dissolution interface subset b_I, as well as their differentials subsets used in the integration of Eq. 14, are also proportioned as:

$$b_{SL} = (1 - \theta_{SIL}) \, b_I \quad \text{and} \quad b_{SIL} = \theta_{SIL} \, b_I \qquad \text{Eq. 18}$$

The Tempkin isotherm expression from Eq. 16 can be substituted into Eq. 18, and this result combined into Eq. 14 to have the entropy energy and chemical energy represented as a surface integrals over only the arbitrary set b_I. In writing out these changes, the transformation from the entropy state function $N(x,t)$ to the configuration entropy function $\Omega(x,t)$, defined as $N(x,t) = k\ln(\Omega(x,t))$ will also be applied[Ref 7], and using the algebraic rules for logarithmic functions, Eq. 14 becomes:

$$\int_{b_I} [\{ \, Tk \, \ln[\Omega_L/\Omega_S] \, (\rho_S V_{SL}) \cdot n_L \, \} \, (1 - \theta_{SIL}) \; +$$

$$\{ \, Tk \, \ln[(\Omega_L/\Omega_S) \, (\Omega_{IS}/\Omega_{IL})](\rho_S V_{SIL}) \cdot n_L \} \, \theta_{SIL} \,] db_I \; =$$

$$- \int_{b_I} \{ [\mu_{LA} c_A + \mu_{LR} c_R + \mu_{LSL} c_{SL} + \mu_{LSA} c_{SA} + \mu_{LSR} c_{SR} - \Delta E_S(M_{So}) \; -$$

$$- \, \mu_S c_S] \, C_{SF}(\rho_S V) \cdot n_L \, (1 - p_{SI0} + p_{SI} kT \ln[C_S] + p_{IL0} + p_{IL} kT \ln[C_L])$$

$$- \, [\mu_{LA} c_A + \mu_{LR} c_R + \mu_{LSL} c_{SL} + \mu_{LSA} c_{SA} + \mu_{LSR} c_{SR} - \mu_{IL} c_{IL} + \mu_{IS} c_{IS} - \mu_S c_S$$

$$- \, \Delta E_S(M_{So})] C_{SF}(\rho_S V) \cdot n_L \} (p_{SI0} + p_{SI} kT \ln[C_S] + p_{IL0} + p_{IL} kT \ln[C_L]) \} db_I \quad \text{Eq.19}$$

Non-Equilibrium Models for Coupled Adsorption and Dissolution Kinetics

The configuration entropy energy and surface velocity terms in the first integral on surface b_I are bounded. And although these terms for "direct and indirect" dissolution pathways may not be spatially continuous at an atomic length scale, the mean value theorem of integral calculus can be applied to define an averaged value of the dissolution interface velocity or, in this case the dissolution mass flux, such that:

$$(\rho_S V_{AVE}) \bullet n_L \left\{ kT \int_{b_I} [\{ \ln[\Omega_L/\Omega_S] \} (1 - \theta_{SIL}) + \{ \ln[(\Omega_L/\Omega_S)(\Omega_{IS}/\Omega_{IL})] \} \theta_{SIL}] db_I \right\}$$

$$= \int_{b_I} [\{ Tk \ln[\Omega_L/\Omega_S] (\rho_S V_{SL}) \bullet n_L \} (1 - \theta_{SIL}) +$$

$$\{ Tk \ln[(\Omega_L/\Omega_S)(\Omega_{IS}/\Omega_{IL})](\rho_S V_{SIL}) \bullet n_L \} \theta_{SIL}] db_I \qquad \text{Eq. 20}$$

Recalling that the subset $b_I(x,t)$ is an arbitrary, but finite area b_I to rigorously satisfy any stochastic conditions on area averaging, the mean value theorem of integral calculus can be applied again to the first term of Eq. 20 to obtain an averaged configuration entropy defined in the following sequence of steps as:

$$[\ln[(\Omega_L/\Omega_S)(\Omega_{IS}/\Omega_{IL})^{\theta_{SIL}}]_{AVE} \; b_I \; =$$

$$[\ln[\Omega_L/\Omega_S] + \ln[(\Omega_{IS}/\Omega_{IL})]^{(\theta_{SIL})}]_{AVE} \; b_I \; =$$

$$[\ln[\Omega_L/\Omega_S]^{(1 - \theta_{SIL})} + \ln[(\Omega_L/\Omega_S)(\Omega_{IS}/\Omega_{IL})]^{(\theta_{SIL})}]_{AVE} \; b_I \; =$$

$$[\{ \ln[\Omega_L/\Omega_S] \} (1 - \theta_{SIL}) + \{ \ln[(\Omega_L/\Omega_S)(\Omega_{IS}/\Omega_{IL})] \} \theta_{SIL}]_{AVE} \; b_I \; =$$

$$\left\{ \int_{b_I} [\{ \ln[\Omega_L/\Omega_S] \} (1 - \theta_{SIL}) + \{ \ln[(\Omega_L/\Omega_S)(\Omega_{IS}/\Omega_{IL})] \} \theta_{SIL}] db_I \right\} \qquad \text{Eq. 21}$$

The same integral operations used to define the above averaged mass flux and entropy terms can be performed on the right hand-side of Eq. 19. With the same order in the steps, an average mass flux would be defined first, and it would be equal to the one defined with the entropy energy integral of Eq. 19, and an averaged chemical plus strain energy density integrand term would be defined second. As discussed previously, an Onsager non-equilibrium model for dissolution rate would use the change in the averaged chemical and strain energy density function across the dissolution front as an energy non-equilibrium metric, and would assume that this energy metric is proportional to the averaged mass flux. This assumption results in a non-equilibrium dissolution rate model, of an Onsager form, that has the following function forms:

$$(\rho_S V_{AVE}) \bullet n_L = L_N C_{SF} \{ - [\mu_{LA} c_A + \mu_{LR} c_R + \mu_{LSL} c_{SL} + \mu_{LSA} c_{SA} + \mu_{LSR} c_{SR}$$

$$- \Delta E_S(\textbf{M}_{So}) - \mu_S c_S] \; (1 - p_{SI0} + p_{SI} kTln[\textbf{C}_S] + p_{IL0} + p_{IL} kTln[\textbf{C}_L])$$

$$- [\mu_{LA} c_A + \mu_{LR} c_R + \mu_{LSL} c_{SL} + \mu_{LSA} c_{SA} + \mu_{LSR} c_{SR} - \mu_{IL} c_{IL} + \mu_{IS} c_{IS} - \mu_S c_S$$

$$- \Delta E_S(\textbf{M}_{So})] \; (p_{SI0} + p_{SI} kTln[\textbf{C}_S] + p_{IL0} + p_{IL} kTln[\textbf{C}_L])\}_{AVE} \qquad \text{Eq.22}$$

where the Onsager "coefficient" L_N is positive, and may have a function of temperature, for example, an Arrhenius dependence may be part of the coefficient. This dissolution rate model is a linear functional of the chemical potential functions of the solid and the liquid and an adsorption isotherm. For low concentrations, these chemical potential functions are typically a logarithmic function of the multi-component species concentrations in the solid $[\textbf{C}_S]$ and in the liquid $[\textbf{C}_L]$, and for which the full set of effective stoichiometric coefficients $\{c_S, c_A, c_R, c_{SL}, c_{SA}, c_{SR}, c_{IL}, c_{IS}\}$ were derived in Eqs. 6, 7, and 10 to 13. In addition to the dependence on the chemical potential functions and stoichiometric coefficients, the dependence on the Temkin adsorption isotherm is explicitly seen in terms of the Temkin parameter set $\{p_{SI0}, p_{SI}, p_{IL0}, p_{IL}\}$ and the kTln[concentration]. Notice that for any surface adsorption kinetics at the interface between the solid and liquid, the reaction pathways for the "direct and indirect" dissolution processes have different energy pathways. These energy pathways are functionally represented by subsets of reactions in which the interface chemical potentials, $\mu_{IL} c_{IL}$ and $\mu_{IS} c_{IS}$, and their other associated stoichiometric coefficients explicitly participate. In fact, this interface dependence will couple by algebraic multiplication the full set of effective stoichiometric coefficients of the chemical energies and the Temkin parameter set. Thus, because of this multiplication of chemical potential functions, with their logarithmic concentration dependence, and the Temkin adsorption isotherm function forms, with their logarithmic concentration dependence, this Onsager non-equilibrium dissolution rate model is a full quadratic in logarithmic functions of both the solid and liquid species' concentrations.

In addition to the above Onsager non-equilibrium dissolution rate model, which should be applicable for numerical regression analysis of dissolution data obtained at near-thermodynamic equilibrium conditions, an alternative non-equilibrium model will be conjectured from the configuration entropy function Ω of Eq. 21. The conceptual basis of a configuration entropy model is similar to that used for the Onsager model, which requires that the functional relationships in the model prevent decreases in the entropy function $\textbf{N}$ for adiabatic processes. In this non-equilibrium dissolution model, the averaged mass flux is assumed functionally proportional to the change in configuration entropy, where the entropy metric is measured by the ratios of the configuration entropy functions. Thus, the averaged mass flux is functionally dependent upon the configuration entropy ratios as given in the first line of Eq. 21 by:

$$(\rho_S V_{AVE}) \cdot n_L = \mathbf{L}_\Omega \left[(\Omega_L/\Omega_S)(\Omega_{IS}/\Omega_{IL})^{\theta_{SIL}} \right]_{AVE} \qquad \text{Eq. 23}$$

where the "coefficient" $\mathbf{L}_\Omega$ is positive, and may have an Arrhenius function of temperature. Of course, the use of configuration entropy is not practical in the sense that no explicit functions forms for the configuration entropy functions, Ω, are readily available as compared to the chemical potential functions of the Onsager model. However, as discussed above, the steps to derive the averaged configuration entropy relationship can be performed to the right-hand side of Eq. 19 for the averaged chemical and strain energy densities. This would again show that the entropy energy rate is equal to the chemical and strain energy rate during the dissolution process. However, that entropy energy is in the **N** function form, which is $\ln[\Omega]$. Thus, the inverse logarithmic relationship must be applied and Ω expressed as $\exp[-\Delta(\text{interface energy})/kT]$. In the case of the configuration entropy ratios of Eq. 23, the function arguments of the exponential function are the averaged chemical and strain energy densities of Eq. 22, divided by "kT" [Ref 4]. Thus, the second non-equilibrium dissolution rate model based on a configuration entropy metric with coupled surface adsorption and dissolution kinetics has function forms given by:

$$(\rho_S V_{AVE}) \cdot n_L = \mathbf{L}_\Omega \left[\exp\{ (\mathbf{C}_{SF}/kT) \{ - [\mu_{LA} c_A + \mu_{LR} c_R + \mu_{LSL} c_{SL} + \mu_{LSA} c_{SA} \right.$$

$$+ \mu_{LSR} c_{SR} - \Delta E_S(\mathbf{M}_{So}) - \mu_S c_S](1 - p_{SI0} + p_{SI} kT \ln[\mathbf{C}_S] + p_{IL0} + p_{IL} kT \ln[\mathbf{C}_L])$$

$$- [\mu_{LA} c_A + \mu_{LR} c_R + \mu_{LSL} c_{SL} + \mu_{LSA} c_{SA} + \mu_{LSR} c_{SR} - \mu_{IL} c_{IL} + \mu_{IS} c_{IS} - \mu_S c_S$$

$$\left. - \Delta E_S(\mathbf{M}_{So})] (p_{SI0} + p_{SI} kT \ln[\mathbf{C}_S] + p_{IL0} + p_{IL} kT \ln[\mathbf{C}_L]) \}_{AVE} \right] \qquad \text{Eq. 23}$$

This dissolution rate model has an exponential function dependence with an argument function that is a linear functional of the chemical potential functions of the solid and the liquid and an adsorption isotherm. Without the surface adsorption isotherm dependence, this dissolution rate model has more functional similarities with those used in electro-chemistry corrosion models[Ref 9, 17, 20] than the previous Onsager model. In fact, had the electric dipole energy term been retained, the function forms would be almost congruent[Ref 4]. For low concentrations, the chemical potential functions are typically a logarithmic function of the multi-component species concentrations in the solid [$\mathbf{C}_S$] and in the liquid [$\mathbf{C}_L$], and for which the full set of effective stoichiometric coefficients $\{c_S, c_A, c_R, c_{SL}, c_{SA}, c_{SR}, c_{IL}, c_{IS}\}$ were derived in Eqs. 6, 7, and 10 to 13. Again, without the surface adsorption isotherm dependence, the logarithmic argument of the exponential function simplifies to just the argument of the logarithmic function, which is the species concentration raised to the power of its effective stoichiometric coefficient. With the adsorption isotherm,

the coupled dependence of the chemical potential functions and stoichiometric coefficients and the Temkin adsorption isotherm is explicitly represented as a multiplication of the Temkin parameter set $\{p_{SIO}, p_{SI}, p_{ILO}, p_{IL}\}$ and the $kT\ln[\text{concentration}]$ and the energy densities. As was the case for the previous Onsager model, notice that for any surface adsorption kinetics at the interface between the solid and liquid, the reaction pathways for the "direct and indirect" dissolution processes have different energy along the two pathways. These energy differences along the pathways are again functionally represented by subsets of reactions in which the interface chemical potentials, $\mu_{IL}c_{IL}$ and $\mu_{IS}c_{IS}$, and their other associated stoichiometric coefficients explicitly participate. As before, this interface dependence will couple as the result of this algebraic multiplication the full set of effective stoichiometric coefficients of the chemical energies and the Temkin parameter set, but in this case the averaged mass flux of dissolution is an exponential interface dependence. Also, the multiplication of chemical potential functions and the Temkin adsorption isotherm function forms, both of which have their logarithmic concentration dependence, cause this configuration entropy dissolution rate model to have a full quadratic in logarithmic functions of both the solid and liquid species' concentrations as its exponential argument. Thus, if adsorption kinetics are at all significant in a multi-component dissolution process, it would be most fortuitous to gather test data over a wide range of control variable test conditions and substantiate by a regression analysis a mono-casual relationship for an idealized single step stoichiometric reaction.

In the case of uranium oxide dissolution response, some of the tests where these types of models are applicable are in Ref. 22 to 26. In Grandstaff, the dissolution test data were interpreted to have a surface adsorption reaction for carbonated water solutions[Ref 22]. In the other uranium oxide tests[Ref 23 – 26], which had un-irradiated uranium oxide and spent fuel uranium oxide dissolution test data, the un-irradiated uranium oxide dissolution rate data were interpreted to have an simple, and expected, oxygen fugacity and Arrhenius temperature dependence in carbonated water solutions. However, the spent fuel dissolution data were significantly different in oxygen and temperature dependence relative to the un-irradiated uranium oxide dissolution data, and this led to the inclusion of spent fuel burn-up as an additional causal regression variable[Ref 2, 24]. No substantiated mechanistic understanding is available to explain the differences in the un-irradiated uranium oxide and the spent fuel dissolution data, although some features suggest a surface adsorption coupling. Other features in these data suggest a radiolysis coupling to the dissolution water chemistry. A radiolysis coupling to the dissolution water chemistry will be approximated in the following brief analysis.

Radiolysis Kinetics Coupled to Dissolution and Adsorption Kinetics

The chemical potential functions and Temkin adsorption isotherm expressions as functions of radiolytic species concentrations $[C_R]$ have been generically

included in the two models of Eq. 22 and Eq. 23. The number of potential radiolytic species created by the gamma, beta, alpha and neutron radiation flux from spent fuel is significant[Ref 14] and a detailed accounting of them will not be provided here. For long time intervals before exposure of a spent fuel surface to an aqueous solution, say several hundreds of years, the only remaining radiation field that will deposit significant radiation energy at a wetted surface is the alpha flux field. This analysis of radiolysis is only to derive the simplest and most ideal case concentration function form. The balance equations for gamma, beta, and alpha radiation transport for a first order approximation are the same funtionally as that for neutron transport[Ref 13]. It is only when numerical evaluations are requested that the details become primary. The physical concept is that a flux of high-energy particles scatter down from their initial state of high kinetic energy to a state of lower kinetic energy by a sequence of collisions. For a high energy radiation flux propagating through an aqueous solution, the collisions produce radiolysis species by ionization, which scatters electron(s) beyond the orbital shell(s) of its host atom/molecule, and by creating electronically excited states, which scatters electrons within admissible orbital shells of its host atom/molecule. The concentration of these species influence the local water chemistry and will augment as well as create oxidation reactions in situations where the nominal water chemistry would be judged benign. In the previous discussion, the radiolysis species concentration was denoted as a row matrix $[C_R]$. The balance equation for the rate of change in concentration of a generic species $[C_R(x,t)]$ with respect to time is given by:

$$\partial[C_R]/\partial\, t = \text{net transport} + \text{flux production} - \text{thermal recovery} + \text{net scattering}$$

Of the four processes that cause changes in the concentration, only a linear flux production and a linear concentration thermal recovery with a Arrhenius temperature dependence will be represented. Thus, the balance equation is:

$$\partial[C_R]/\partial\, t = \rho_R \sigma_R\, F - \Gamma_R\, [C_R]\exp(\, -Q_R/kT) = \rho_R \sigma F - \Gamma_R\, [C_R]\exp(\, -Q_R/kT) \quad \text{Eq. 24}$$

where $\rho_R \sigma_R\, F$ is the flux production rate, and ρ_R is the local source density for the production of species $[C_R]$, times the cross-section σ_R for a collision, times the radiation flux density F, and the recovery rate is, $\Gamma_R[C_R]\exp(\, -Q_R/kT)$, where Γ_R is a constant times the species concentration $[C_R]$ times the Arrhenius temperature dependence $\exp(\, -Q_R/kT)$. For a quasi-steady radiation flux, the quasi-steady state species concentration at the dissolution front is given as:

$$[C_R(t)] = (\rho_R \sigma_R\, F(t)\, /(\, \Gamma_R \exp(-Q_R/kT)) = (\rho_R \sigma_R\, F(t)\, \exp(Q_R/kT))/\, (\, \Gamma_R) \quad \text{Eq. 25}$$

For a spent fuel with a burn-up of $Bu(t_0)$ at the discharge time t_0, the alpha radiation flux from the SF actinides at a later time t can be roughly estimated as $F(t) = K_{R\alpha}\, Bu_\alpha(t)$. Thus, the alpha radiolysis species concentration is also SF

burn-up dependent but with a long half-life decay factor, which for alpha decay is slow, and is approximately given as:

$$[C_R(t)] = (\rho_R \sigma_R \; K_{R\alpha} \; Bu_\alpha(t)exp(Q_R/kT))/(\Gamma_R) = K_{CR\alpha} \; Bu_\alpha(t)exp(Q_R/kT) \quad \text{Eq. 26}$$

Looking at the two models developed in Eq.22 and Eq. 23, the radiolysis species concentration of Eq. 26 would be used to evaluate the radiolysis chemical potential function $\mu_{LR}c_R$ times its effective stoichiometric coefficient and provides a contribution to the chemical energy changes at the dissolution front. Using the chemical potential function from Eq. 6, this term is given by:

$$\mu_{LR}c_R = \mu_{LR0}c_R + kTln[C_R(t)] = \mu_{LR0}c_R + kTln[K_{CR\alpha} \; Bu_\alpha(t)exp(Q_R/kT)]$$

$$= \mu_{LR0}c_R + Q_Rc_R \; ln[K_{CR\alpha}] + c_R \; kTln[Bu_\alpha(t)] \quad\quad \text{Eq. 27}$$

Thus, the radiolysis species, for this approximation, has a SF burn-up dependence that is functionally similar to the burn-up dependence of the solid species concentration $[C_S]$ of Eq. 6 and the solid to liquid species ionic concentration $[C_{SL}]$ of Eq. 7. Thus, if one identifies by a numerical regression analysis over a set of dissolution rate data that a causal dependence exists on the aggregate burn-up variable **Bu**, the mechanistic origin of the dependence would probable require additional dissolution test. Assuming that these tests were performed in an augmented external radiation field $F_{\alpha ext}(t)$ that is additive to the intrinsic radiation field of the spent fuel then, Eq. 27 would be of the form:

$$\mu_{LR}c_R = \mu_{LR0}c_R + Q_Rc_R \; ln[K_{CR\alpha}] + c_R \; kTln[Bu_\alpha(t)] + c_R \; kTln[F_{\alpha ext}(t)] \quad \text{Eq. 28}$$

and the radiation field of the dissolution tests could be varied independently from the intrinsic radiation field of the fuel. This may isolate the aggregate spent fuel burn-up dependence in the solid from that in the aqueous solution on the dissolution response in test data. Then, numerical regression analysis[Ref 26] of these data may isolation causality of any burn-up dependence mechanisms.

Summary
Two theoretical expressions are developed for the dissolution rate response of a multi-component solid that has surface adsorption kinetics and radiolysis kinetics when wetted by a multi-component aqueous solution. An application for this type of dissolution response is the performance evaluation of multi-component spent nuclear fuels(SNFs) for long term interim storage and for geological disposition. The theory is formulated for a solid/liquid phase change discontinuity that propagates at a quasi-steady velocity. The chemical reaction steps occurring at the solid-liquid interface are assumed to control the rate of dissolution; rather than the rate limited by diffusion to the solid-liquid interface. The non-equilibrium thermodynamic analysis is primarily developed from the conservation of the energy rate equation across a solid-liquid phase change discontinuity. This energy rate equation contains the internal energy functionals of classical thermodynamics for both the SNFs' solid state, an idealized

interface, the adjacent liquid state, and the radiolytic chemical species. Thus, the derived equations for both dissolution rate responses are not represented in terms of the Gibb's thermodynamic potential, which typifies most existing physical chemistry thermodynamic theories for dissolution rate expressions. There are two primary assumptions used to derive the two functional dissolution rate expressions. The first is that the irreversible production rate of entropy across the solid-liquid phase change discontinuity is proportional to the propagation velocity of the solid-liquid interface. The second is that the surface adsorption kinetics, which determines the active area subsets where dissolution occurs, are dependent on some solid-liquid adsorption isotherm and radiolytic chemical species. For purposes of illustration a modified Temkin adsorption isotherm was selected. For this case, where the quasi-steady dissolution rate is dependent on surface adsorption kinetics, there is also an assumption that the surface density of active dissolution sites is at a thermodynamic quasi-equilibrium, asymptotically stationary, state. The dissolution rate expression has a functional dependence on adsorption isotherm kinetics, radiolysis kinetics, and thermodynamic chemical potentials. For idealized dissolution processes that depend on surface adsorption and radiolysis kinetics, approximations are made to obtain a theoretical rate expressions for empirical and/or regression analysis of data. Based on this analysis, the use of other adsorption isotherms, such as a Langmuir and/or Freundlich isotherms, should also be considered when conjectures are made to formulate alternative theoretical rate expressions. The coupled kinetics from adsorption, from radiolysis, and from dissolution processes provide a challenge to experimentally isolate, and then assign causal relationships by numerical regression analyses on available sets of un-irradiated and spent nuclear fuel dissolution data.

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